

# Synthetic Organic Chemicals

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## *Organic Chemicals as Rubber Accelerators*

THE extensive use of organic compounds as accelerators for the vulcanization of rubber may be claimed to date from 1914. Prior to that time, however, a number of inorganic substances, for example, litharge, magnesium oxide and carbonate, calcium oxide and hydroxide, basic lead carbonate, sodium and ammonium hydroxides, and antimony polysulphides, had been known to hasten the process of vulcanization. Also as early as 1906 aniline was compounded with rubber for the specific purpose of hastening vulcanization. In 1907 Oenolager introduced the use of thiocarbanilide, and in 1912 Spence used piperidine.

However, the first public disclosure of a specific process using organic chemicals as rubber accelerators was in a patent granted to Bayer & Company in 1913, claiming the use of piperidine and its homologues. Closely following this aliphatic amines were used, and also the condensation products of these amines with carbon disulphide, resulting in the formation of dithiocarbamates, e.g.,

- (a)  $2(\text{CH}_3)_2\text{NH} + \text{CS}_2 = (\text{CH}_3)_2\text{N} - \text{CS} - \text{S NH}_2(\text{CH}_3)_2$   
(Dimethylamine) (Dimethylammonium Dimethyl Dithiocarbamate)
- (b)  $2 \text{C}_5\text{H}_{10}\text{NH} + \text{CS}_2 = \text{C}_5\text{H}_{10}\text{N} - \text{CS} - \text{S NH}_2\text{C}_5\text{H}_{10}$   
(Piperidine) (Pentamethylene Piperidine Dithiocarbamate)

Since bases in general were found to be good accelerators, Bayer & Company applied for a patent for the employment of such ammonia derivatives of nitrogenous bases as possessed a dissociation constant higher than  $1 \times 10^{-8}$ .

Constant experimentation has been carried on from the date of these early patents, and since 1914, the numbers of organic compounds which have been found capable of accelerating the vulcanization of rubber has greatly increased. For convenience they may be grouped into the following classification. This list is by no means complete, but merely covers those compounds which are, or have been, more commonly used as accelerators in rubber practice.

### I. Condensation products of ammonia and organic bases with aldehydes.

In this class may be listed a number of so-called Schiff's Bases of the general formula  $\text{R} - \text{CH} = \text{NR}'$ , where  $\text{R}$  or  $\text{R}'$  may be alkyl or aryl radicals. The most satisfactory products are those formed by the condensation of an aliphatic aldehyde with an aromatic amine.

Compounds, other than Schiff's Bases, falling into this class are hexamethylenetetramine, aldehyde ammonia, and furfuralamide.

### II. Aliphatic and aromatic amines.

The most common chemicals belonging to this class are piperidine, aniline, alkyl anilines, phenylenediamines, and

diphenylamine. With the possible exception of aniline, the free amines are not very extensively used in ordinary practice.

### III. Guanidines.

The following guanidines are used quite extensively: diphenyl, diorthotolyl, triphenyl, phenyl orthotolyl, and tritolyl.

### IV. Nitroso derivatives.

For example, para-nitrosodimethylaniline, para-nitrosodiphenylamine, and paranitrosophenol can also be used.

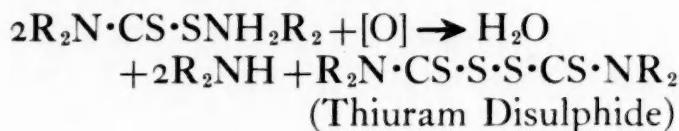
### V. Alkaloids.

Brucine and narcotine have been shown to be accelerators, but the price prohibits their use. However, a commercial by-product from the manufacture of quinine from cinchona, known commercially as quinoidine, has been recommended and used as an accelerator. The amount of this material available is quite definitely limited by the production of quinine.

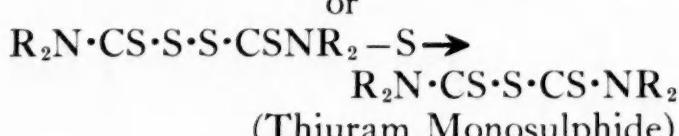
### VI. Carbon disulphide derivatives of aliphatic and aromatic amines.

This class includes the alkaline and metallic salts of substituted dithiocarbamic acid (e.g., ammonium and substituted ammonium salts of dialkyldithiocarbamic acids or zinc dialkyl dithiocarbamates), esters of substituted dithiocarbamic acids, thiocarbanilide and other substituted thioureas, and the thiuram mono- and disulphides.

These last named compounds are prepared from the dithiocarbamates by mild oxidizing agents, thus:



or



### VII. Carbon disulphide derivatives of aliphatic alcohols.

This class includes the xanthates and xanthogenates, e.g.,  $C_2H_5 \cdot CS \cdot SK$   
(Potassium Ethylxanthate) and  $C_4H_9O \cdot CS \cdot S \cdot CS \cdot OC_4H_9$   
(Dibutyl Xanthogenate)

### VIII. Salts of thioacids.

Thiocarbonates and thiobenzoates are known to have accelerating properties.

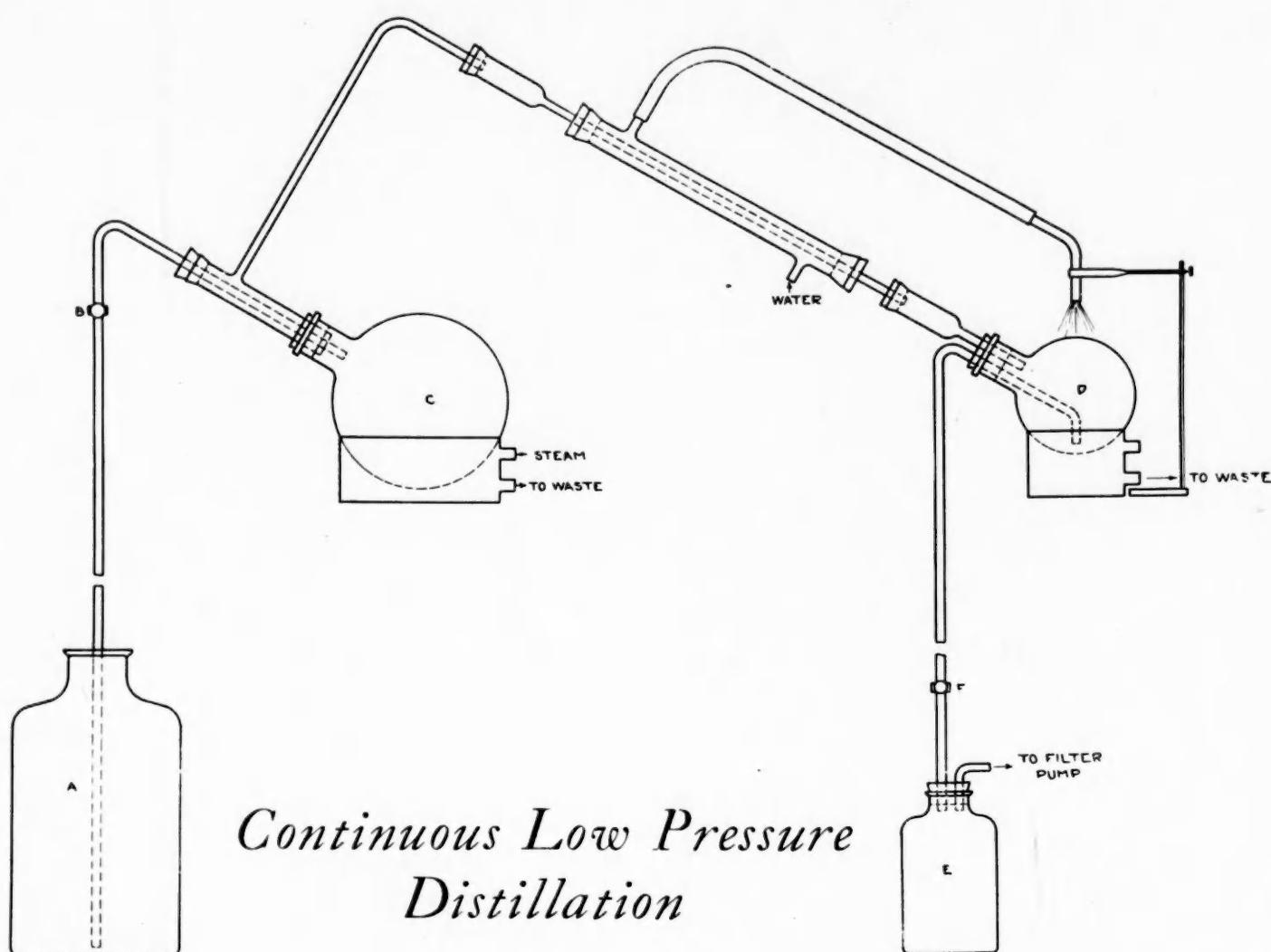
### IX. Thiazole derivatives.

Mercaptobenzothiazole and some of its derivatives are extensively used.

At first it might be thought that the only factor governing the development of new accelerators would be to find the "ultra rapid" product which would give a satisfactory state of vulcanization in a minimum of time. This is not the case, for it would be impossible to mix such a product into rubber (a process conducted on heated rolls) without causing vulcanization during the mixing operation. In fact, it is common practice in the rubber industry deliberately to dilute very active accelerators with inert diluents in order to avoid this pre-vulcanization during milling. In passing, however, it should be mentioned that rapid accelerators are used in cases where vulcanization and compounding are to be carried out at low temperatures.

The activity of different accelerators varies considerably when they are compared directly in the same rubber mix. The most active members, e.g., thiuram and thiocarbamic acid derivatives, are known as "ultra accelerators," and they are capable of bringing about vulcanization in quite a reasonable period of time, even in the absence of sulphur, providing zinc oxide is present in the mix. This last point at once suggests that it is not advisable, therefore, to compare one class of accelerators directly with another in

(Continued on page 4)



### *Continuous Low Pressure Distillation*

**I**N chemical laboratories, it frequently becomes necessary to distill or evaporate rather large quantities of solvents which contain small amounts of non-volatile constituents. To accomplish this result with a minimum expenditure of time, the apparatus sketched here has been found useful. It consists of a large container (A); a 12-liter flask (C) on a steam pot; a 3-liter flask (D) which serves as part of the condensing system and also as a temporary receiver; and a 2-liter bottle (E), which is the receiver. The screw clamp (B) regulates the rate of flow of liquid into the distilling flask, while the second clamp (F) allows the receiver to be changed whenever necessary without interrupting the distillation.

At the beginning, both screw clamps are opened, steam is introduced into the steam pot under C, and the filter pump is connected to the receiver (E). Screw

clamp (B) is regulated so the flow of liquid from A to C is approximately equal to the rate of distillation. When the receiver (E) has filled with distillate, F is closed, and the distillate accumulates in the flask (D) until the bottle can be emptied and evacuated again.

The steam pot under C can, of course, be replaced by a salt or oil bath. When low boiling solvents, such as ether or acetone, are to be distilled, reduced pressure is unnecessary, so the container (A) may be placed above C and the solvent siphoned into the distilling flask. The tube leading from D to E is then turned so the end in flask D points upward. When the flask has filled, the tube is reversed, connected to the receiver (E), and the distillate brought over by means of the filter pump. The receiving flask (D) is thus emptied without disconnecting it from the apparatus and without stopping distillation.

(Continued from page 2)

the same rubber mix since the presence of certain compounding ingredients greatly influences the results. It is this very fact that has led to the development of so many new accelerators, for while a certain class of compounds is satisfactory for one type of rubber mix, another class is better suited for a totally different mix. As an example of this case, it has been found that many accelerators work satisfactorily in the presence of 3 parts of sulphur per 100 parts of rubber, while others require at least 6 or 7 parts of sulphur in order to bring about a correct result. Again, the presence of much or little zinc oxide in a rubber mix entirely alters the behavior of most accelerators since this material behaves as an activator. On the other hand, carbon black, a substance used in large proportions in the compounding of automobile tires, is found to have a retarding effect on most accelerators, and much has been done recently in the development of new accelerators which work satisfactorily in the presence of this material. Lastly, the presence of reclaimed rubber modifies the activity of most accelerators.

Not only have accelerators hastened the process of vulcanization, but they have, in general, made it possible to bring about vulcanization with the use of less sulphur. This has greatly decreased the "blooming effect," so noticeable in rubber articles of two decades ago, by lowering the amount of uncombined sulphur in the rubber. It is now possible to mix a number of organic dyes with rubber to produce the beautiful array of colored articles of today, because accelerators have brought about vulcanization at lower temperatures. With high temperature vulcanization their production would be quite impossible. Lastly, it may be claimed that accelerators have greatly improved the tensile properties of manufactured rubber articles.

### Eastman Organic Chemicals as Analytical Reagents

#### XIII Reagents for Zinc

##### DIPHENYLBENZIDINE

Cone and Cady, J.A.C.S. 49, 356 (1927)

Three or four drops of a solution containing one gram of diphenylbenzidine in 100 cc. of concentrated sulfuric acid, are used as an indicator in titrating zinc solutions with potassium ferricyanide. A blue coloration appears as soon as the titration is begun and persists until the endpoint is reached, at which time it changes to pale green. The solution can be back-titrated if necessary. The optimum temperature is 40-60° C.

##### 8-HYDROXYQUINOLINE

Berg, Z. Anal. Chem. 71, 171 (1927)

Zinc is precipitated quantitatively from weak acetic acid solutions containing sodium acetate by adding 2% alcoholic solution of 8-Hydroxyquinoline to the hot solution. The magnesium compound remains in solution. The precipitated zinc compound is washed with hot water, dried at 125°, and weighed. It contains 18.49% zinc. By carrying out the precipitation in alkaline, ammoniacal, or alkaline-tartrate solutions, separation from other metals can be obtained.

##### RESORCINOL

Yoe, Photometric Chem. Analysis (1928)

A sample containing about 0.1 mg. of zinc is dissolved and ammonium hydroxide added until the precipitate redissolves. The solution is diluted to 100 cc. and 2 cc. of 5% resorcinol in alcohol is added. The blue color is compared with a standard sample, containing about the same quantity of zinc treated in the same manner. If the comparison is not made at once, the solution should be protected from air by a layer of Nujol.